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COMPARISON OF THE WYMARK CO₂ RESERVOIR WITH THE MIDALE BEDS AT THE WEYBURN CO₂ INJECTION PROJECT

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Executive Summary

The Devonian carbonates of the Duperow Formation on the western flank of the Williston Basin in southwest Saskatchewan contain natural accumulations of CO₂, and may have done so for as long as 50 m.y. in the views of some investigations. These carbonate sediments are characterized by a succession of carbonate cycles capped by anhydrite-rich evaporites that are thought to act as seals to fluid migration. The Weyburn CO₂ injection site lies 400 km to the east in a series of Mississippian carbonates that were deposited in a similar depositional environment. That natural CO₂ can be stored long-term within carbonate strata has motivated the investigation of the Duperow rocks as a potential natural analogue to storage of anthropogenic CO₂ that may ultimately provide additional confidence for CO₂ sequestration in carbonate lithologies. For the Duperow strata to represent a legitimate analog for Midale injection and storage, the similarity in lithofacies, whole rock compositions, mineral compositions and porosity with the Midale Beds must be established. Previous workers have demonstrated the similarity of the lithofacies at both sites. Here we compare the whole rock compositions, mineralogy and mineral compositions. The major mineral phases at both locales are calcite, dolomite and anhydrite. In addition, accessory pyrite, fluorite and celestine are also observed. The distribution of porosity in the Midale Vuggy units is virtually identical to that of the Duperow Formation, but the Marly units of the Midale have significantly higher porosity. The Duperow Formation is topped by the Dinesmore evaporite that is particularly rich in anhydrite, and often contains authigenic K-feldspar. The chemistry of dolomite and calcite from the two localities also overlaps. Silicate minerals are in low abundance within the analyzed Duperow samples, < 3 wt% on a normative basis, with quartz the only phase identifiable in x-ray diffraction patterns. The Midale Beds contain significantly higher silica/silicate concentrations, but the silicate minerals observed, K-feldspar and quartz, are unlikely to participate in carbonate mineral precipitation due to the absence of alkaline earths. Hence, physical and solution trapping are likely to be the primary trapping mechanisms at both sites. Given the similarity of mineral constituents, whole rock and mineral chemistry, reactive transport models developed for the Weyburn site should also be applicable to the Duperow lithologies.

1. Introduction

Exploratory drilling in the western Williston Basin encountered natural accumulations of CO₂, N₂ and He within the clastic strata of the Cambrian Deadwood Formation and in the carbonates of the Middle Devonian Winnipegosis and Souris River and Upper Devonian Duperow Formations. These natural CO₂ occurrences are found about 400 km west of the site of the IEA Weyburn CO₂ Storage and Monitoring Project (Figure 1), and in some cases contain as much as 80 mol% CO₂ within the Middle and Upper units of the Wymark Member (Lane, 1987). At the Weyburn Field CO₂ is being injected into Mississippian Midale Beds, a succession of cyclic carbonate deposits formed in a shallow setting with porous intervals capped by evaporite units of variable thickness that are thought to be effective seals to fluid migration. Previous workers have demonstrated the depositional and stratigraphic similarity between the Midale Beds

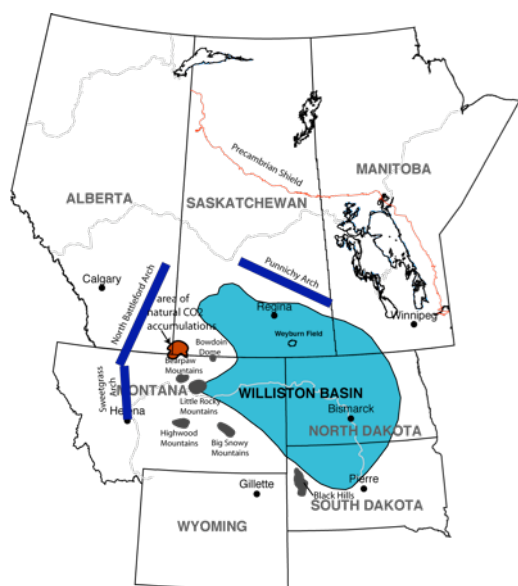


Figure 1. Map showing the location of the Williston Basin and natural CO₂ occurrences (shown in red) in southwestern Saskatchewan relative to the location of the Weyburn CO₂ injection site (From Lake and Whittaker, 2006)

and the Devonian carbonates to the west (cf., Lake and Whittaker, 2006 and references therein). Given the similarity in basinal environment and geological framework, the CO₂ occurrences in Devonian carbonates of southwestern Saskatchewan represent a natural analogue for the Weyburn CO₂ injection site, and the capacity of these lithologies to trap CO₂ on geologic timescales may add confidence to long-term storage of anthropogenic CO₂. The legitimacy of the Devonian carbonates as an analog for the Midale beds was established by previous petrographic and sedimentological analysis (Lake and Whittaker, 2003; 2006). Here we perform a similar analysis comparing the whole rock and mineral chemistry of the Midale and Duperow Formations.

The mineral and whole rock chemistry of the Midale and Duperow units have been studied in detail. Durocher et al. (2003) obtained XRF-ICPMS analysis of the major and trace element geochemistry of a large number of Midale samples, complementing these data with XRD and electron microprobe data to quantify mineral assemblages and chemistry. Normative mineral abundances were calculated using a least squares analysis program, LPNORM (de Caritat et al., 1994), which fits mineral abundance through regression of mineral chemistry and whole rock compositions. Ryerson and Johnson (2010) performed a similar analysis of the Duperow samples studied previously by Lake and Whittaker (2003). Here we compare the results of these investigations to further evaluate the Duperow natural analog to Weyburn CO₂ injection.

2. Results

2.1 Petrography

The Duperow and Midale samples are largely limestones and dolostones with a simple mineralogy consisting of calcite, dolomite and anhydrite. Pyrite and fluorite are also common accessory minerals, and some anhydrite-rich assemblages contain celestine as well. The abundance of silicate minerals in the Duperow samples is low, < 3 wt% for the samples studied by Ryerson and Johnson (2010). Durocher et al. (2003) analyzed a larger suite of Midale samples and found normative quartz concentrations as high as 30 wt% in some samples. The carbonates from both locations can be roughly classified as dolomitized

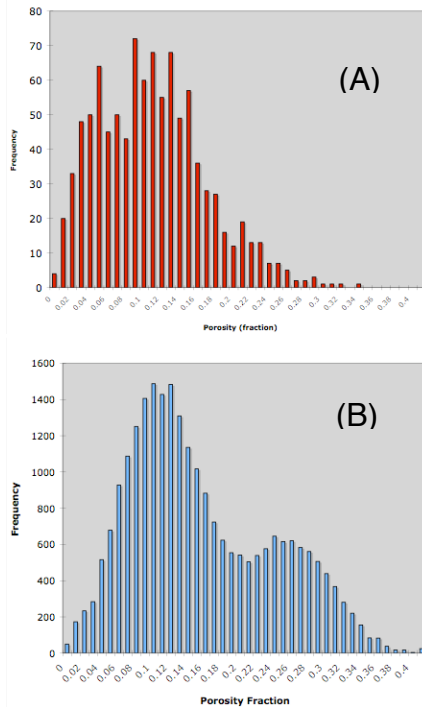


Figure 6. Porosity data for the Duperow Formation and Midale beds at Weyburn. Midale peak at 0.12 is the Vuggy unit, that at 0.26 is the Marly unit. Data from the Ministry of Energy and Resources.

mudstones, fossiliferous limestones, pelletal lime mudstones and evaporites. Lake and Whittaker (2003, 2006) demonstrated the petrographic similarity of the samples from Duperow and Midale, and photomicrographs for the major petrographic types are reproduced in Figures 2-5 along with synoptic backscattered electron maps for the corresponding Duperow samples from Ryerson and Johnson (2010). The petrographic characteristics of both sample suites are consistent with their common depositional setting.

2.2 Porosity

The ability to store and trap natural and anthropogenic CO₂ is directly related to the distribution of porosity in the reservoirs. This is especially true in the case of physical entrapment or solution trapping where the CO₂-bearing fluid/gas phase is free to migrate. Porosity data, obtained from the Ministry of Energy and Resources (courtesy of Erik Nickel) are shown in Figure 6. The Midale beds display a bimodal porosity distribution associated with the lower porosity Vuggy (average ~ 0.1) and the higher porosity Marly units (average ~ 0.25). While the data for the

Duperow formation are less abundant, the porosity closely resembles that of the Vuggy unit at Weyburn with an average of ~ 0.12 with some values reaching as 0.35.

2.3 Whole Rock Geochemistry

The major and trace element data for the Midale and Duperow units are taken from Durocher et al. (2003) and Ryerson and Johnson (2010), respectively, and are not tabulated here. Given the primary mineralogy, consisting of calcite, dolomite, anhydrite and variable concentrations of silicate minerals, the overall chemical variability is best displayed as variations in CaO, MgO, SO₂ and SiO₂ (Figure 7). Since

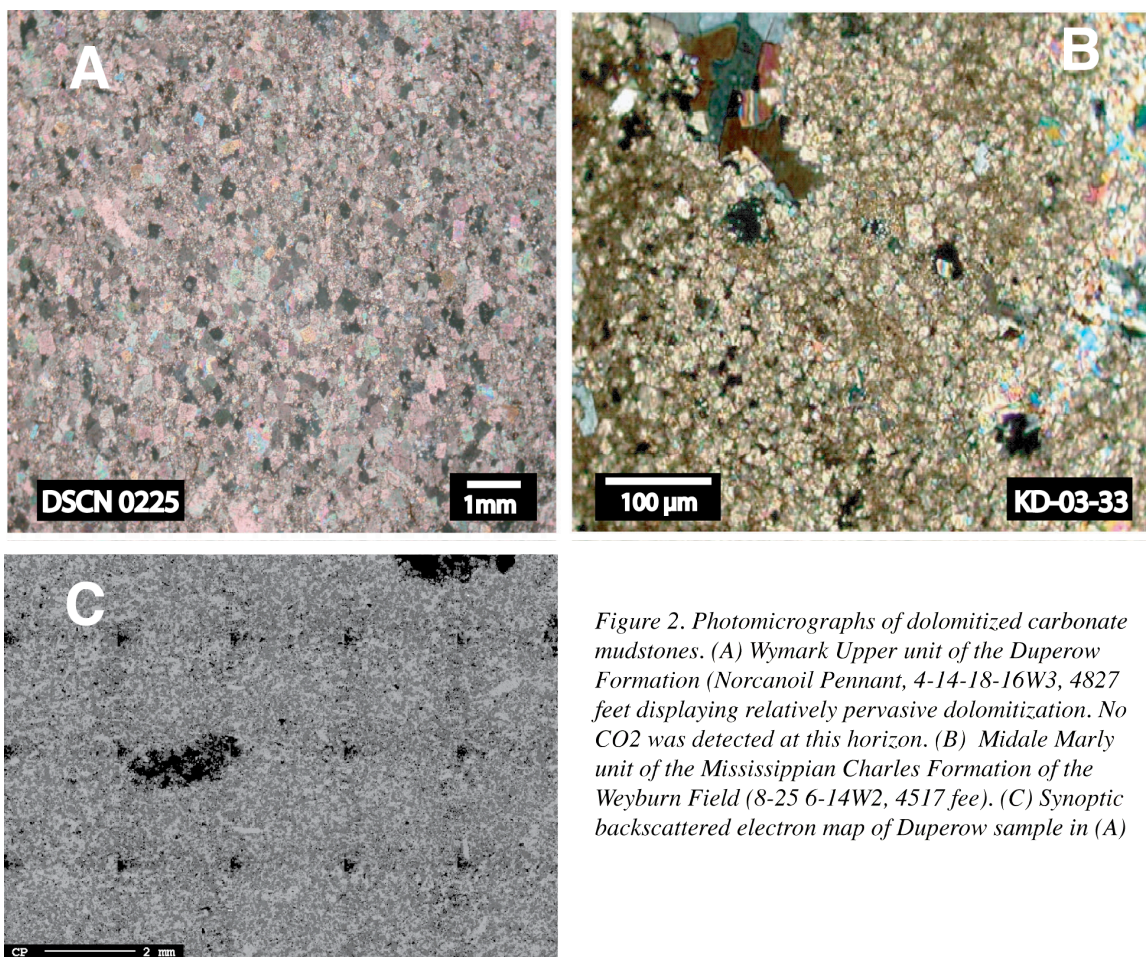


Figure 2. Photomicrographs of dolomitized carbonate mudstones. (A) Wymark Upper unit of the Duperow Formation (Norcanoil Pennant, 4-14-18-16W3, 4827 feet displaying relatively pervasive dolomitization. No CO₂ was detected at this horizon. (B) Midale Marly unit of the Mississippian Charles Formation of the Weyburn Field (8-25 6-14W2, 4517 feet). (C) Synoptic backscattered electron map of Duperow sample in (A)

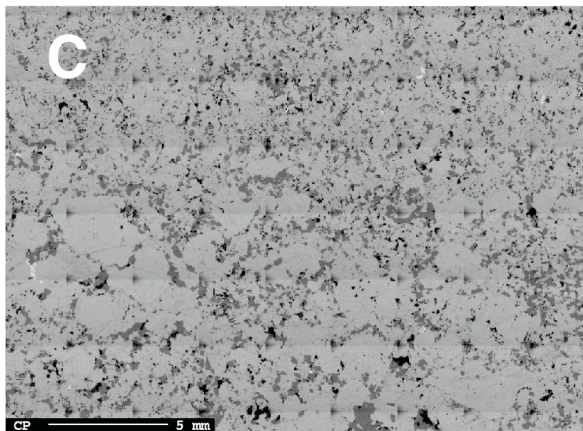
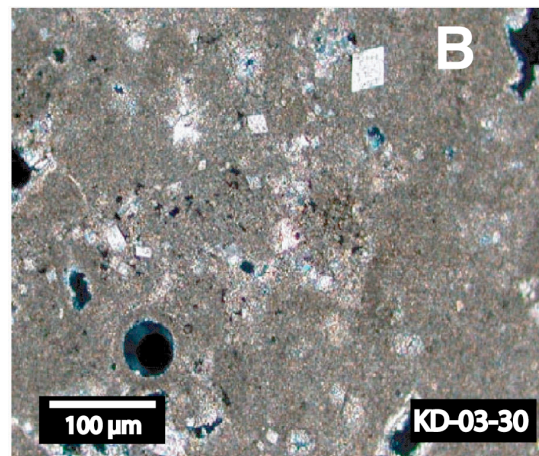
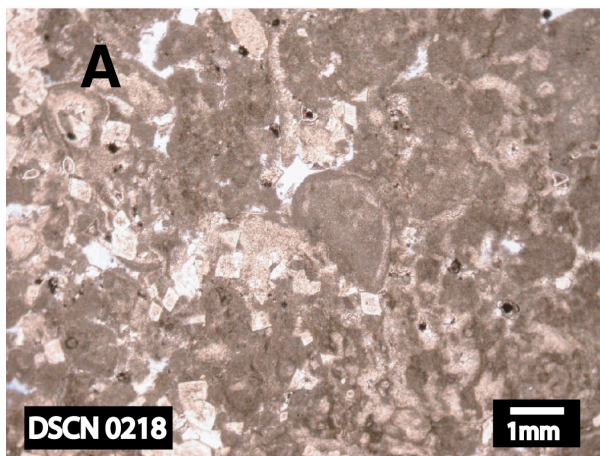


Figure 3 - Photomicrographs of fossiliferous lime mudstones. (A) Wymark Middle unit of the Devonian Duperow Formation (Imp et al Battle Cr. 4-31-3-26W3, 5632 feet. This reservoir layer contain >80 mol% natural CO₂. (B) KD-03-30 is from the Midale Vuggy unit of the Weyburn Pool (14-30-6-13W2, 4496 feet . (C) Synoptic backscattered electron map of Wymark sample (A)

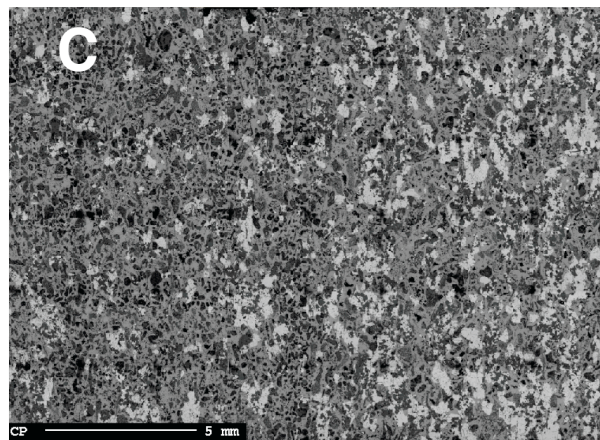
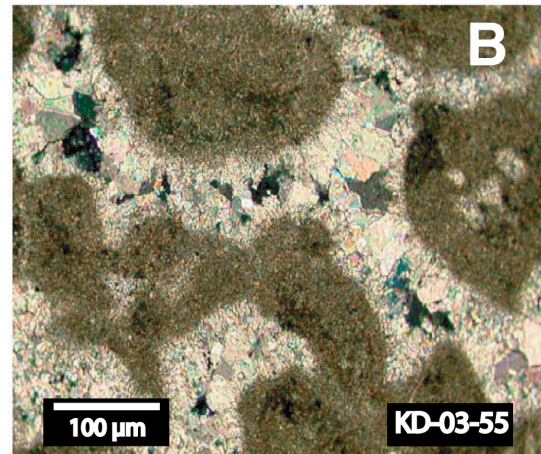
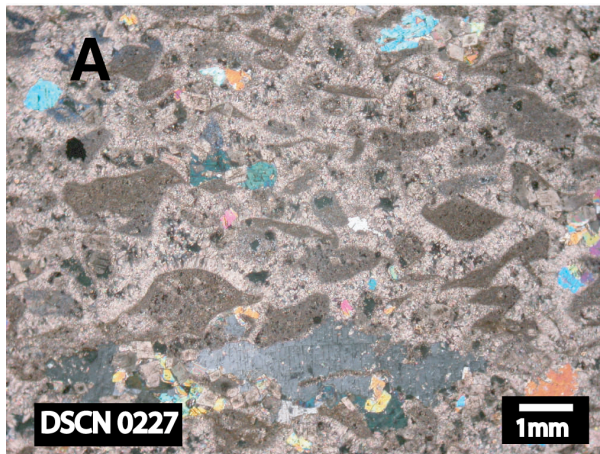


Figure 4. Photomicrograph of peloidal lime mudstones. (A) Wymark Middle unit of the Duperow Formation (T.W. Eastend Cr #1 15-11-6-20W3, 6141 ft). This horizon contains 10 mol% natural CO₂. (B) Midale Vuggy unit of the Weyburn field (8-36-6-13W2, 4476 ft). (C) Synoptic backscattered electron map of Wymark sample (A).

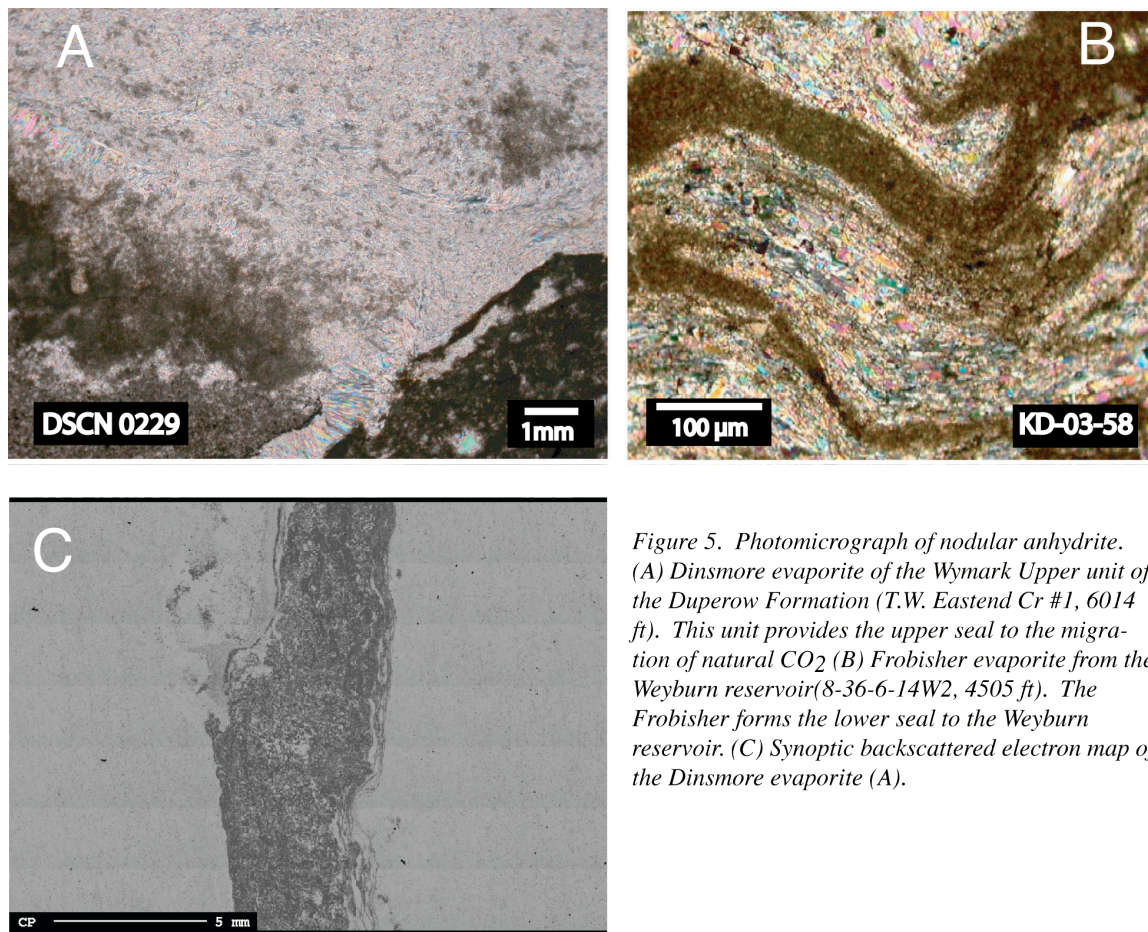


Figure 5. Photomicrograph of nodular anhydrite. (A) Dinsmore evaporite of the Wymark Upper unit of the Duperow Formation (T.W. Eastend Cr #1, 6014 ft). This unit provides the upper seal to the migration of natural CO₂ (B) Frobisher evaporite from the Weyburn reservoir (8-36-6-14W2, 4505 ft). The Frobisher forms the lower seal to the Weyburn reservoir. (C) Synoptic backscattered electron map of the Dinsmore evaporite (A).

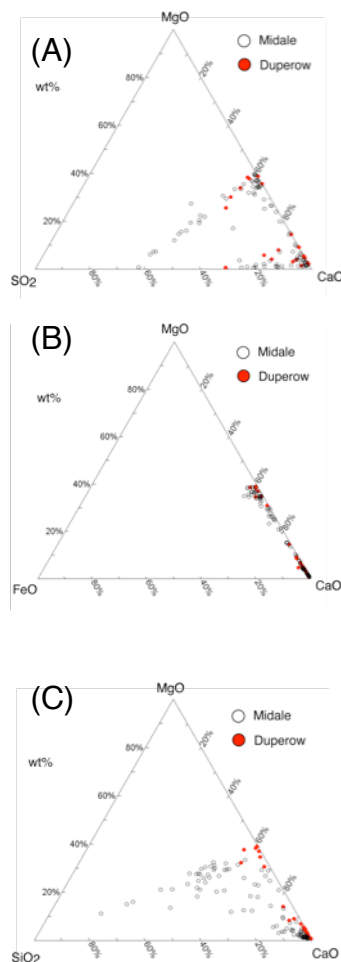


Figure 7. Whole rock compositions of Midale (Durocher et al., 2003) and Duperow samples (Ryerson and Johnson, 2010).

Beds and Duperow Formation (Durocher et al., 2003; Ryerson and Johnson, 2010, respectively), and are not tabulated here. The major carbonate endmember components are calcite, dolomite and ankerite, allowing the variation in calcite and dolomite chemistry to be displayed on the Ca-Mg-Fe ternary in terms of cations (Figure 8). The carbonates from the Midale Beds lie almost entirely along the Ca-Mg join consistent with low concentrations of Fe in these carbonates. The Duperow analyses are similarly restricted to the Ca-Mg join, but there is a small population of samples trending to higher Fe concentrations toward ankerite. As the whole rock chemistry displays little variation in FeO concentration, the higher Fe-dolomites from Duperow

anhydrite (CaSO_3) was the major sulfur-bearing phase, all sulfur was “oxidized” to yield SO_2 to simplify comparison. The variation in CaO-MgO- SO_2 clearly displays the mixing of calcite, dolomite and anhydrite, with essentially all analyses falling in compositional region defined by these phases (Figure 7a). The Midale data extends further toward the CaO- SO_2 join, indicative of a larger fraction of evaporite samples in that data set. The FeO concentrations in both suites are similar (Figure 7b). The range of Duperow samples is much more restricted in terms of CaO-MgO- SiO_2 lying along the CaO-MgO join (Figure 7c). The Midale samples in general contain a higher proportion of silica than the Duperow, and this is shown by the large number of samples falling on a join radial to the SiO_2 apex, consistent with a higher detrital component in the Midale samples. It is difficult to assess whether the higher SiO_2 concentrations represents sampling bias or a true difference between the depositional environments.

2.4 Carbonate Mineral Chemistry

Carbonate mineral chemistry was determined by electron microprobe analysis for the Midale

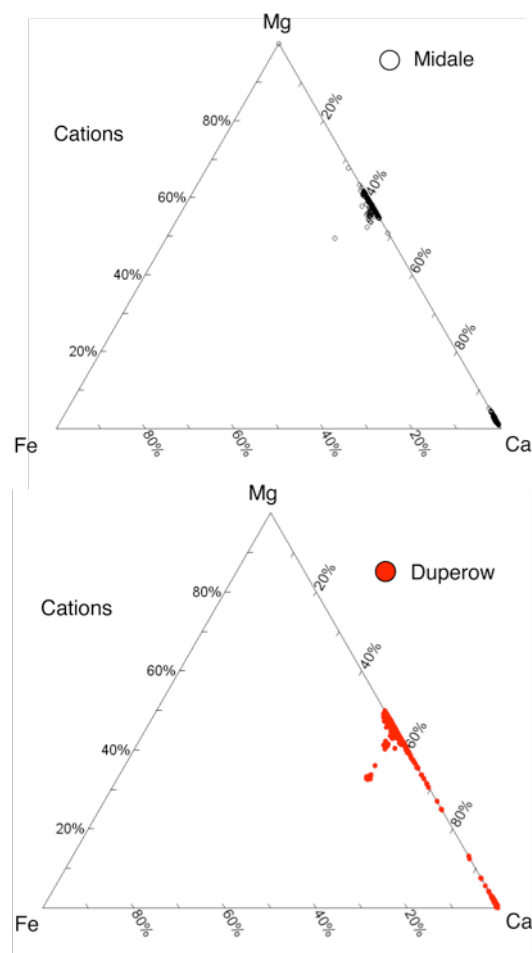


Figure 8. Electron microprobe analysis of carbonate minerals from the Midale Beds (Durocher et al., 2003) and the Duperow Formation (Ryerson and Johnson, 2010).

likely reflect higher density of sampling, including Fe-rich rim compositions from dolomites adjacent to pores (Figure 9). These rim compositions likely reflect growth from late stage fluids enriched in incompatible elements. The sampling of Fe-rich dolomites from the Duperow is also displayed in histograms of the $Mg/(Mg+Ca)$ ratio for carbonate compositions as a “tail” toward lower values reflecting the substitution of Fe for Mg (Figure 10).

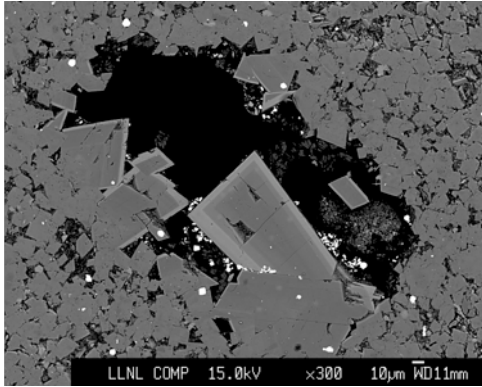


Figure 9. Zoned dolomite growing into a pore in sample 10-32-183 W3M 4746. This horizon contained no natural accumulations of CO_2 .

thin carbonate cycles intercalated with anhydrite-rich evaporates. The carbonates are primarily limestones and dolostones, rich in calcite and dolomite, with variable amounts of silicate minerals and accessory pyrite, fluorite and celestine. Petrographic analysis established the correspondence of specific lithofacies at both sites. The porosity distributions are similar, although the Marly unit of Midale beds does have a significantly higher porosity than carbonates of the Duperow formation. The major element and mineral chemistry of the two stratigraphic successions is also similar. The one compositional factor distinguishing the successions is the higher concentration of silica and silicate minerals in the Midale beds. It should be noted that quartz and K-feldspar are the only silicate minerals identified in thin section in the Duperow or Midale Beds. Silicate minerals rich in alkaline earths, such as plagioclase, appear in normative calculations (Durocher *et al.*, 2003) but have not been identified in thin section. Mineral trapping of CO_2 will be largely dependent upon the dissolution of alkaline earth-bearing silicate minerals to provide the cations necessary for formation of carbonates. The absence of such minerals precludes long-term mineral trapping

2.5 Summary

The Mississippian Midale Beds and Devonian Duperow Formations were deposited under similar environmental conditions producing a succession of

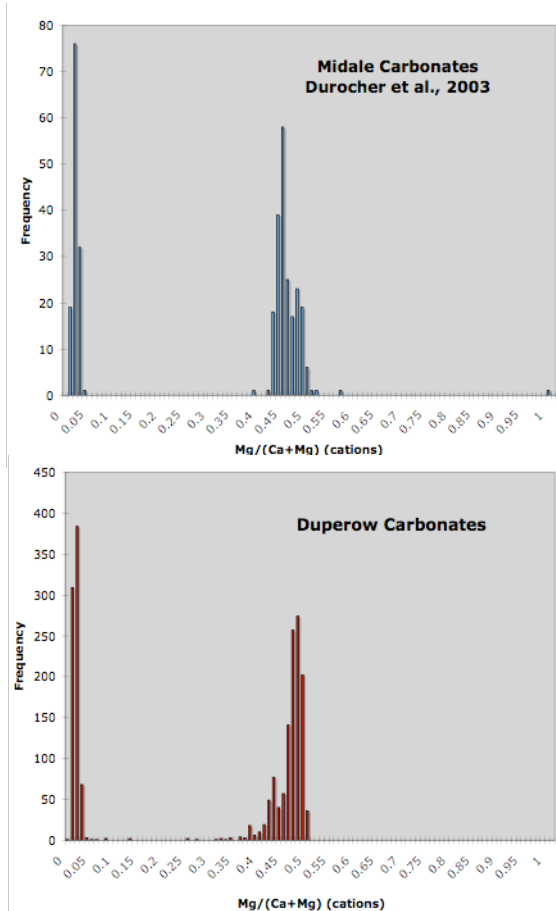


Figure 10. Histogram of $Mg/(Ca+Mg)$ on a cation basis for the carbonates from the Midale beds (Durocher *et al.*, 2003) and the Duperow Formation (Ryerson and Johnson, 2010).

at either site. That the concentration of silicate minerals is higher in the Midale Beds will not enhance the potential for mineral trapping over that of the Duperow due to the nature of the silicate minerals present.

The Duperow Formation in which natural accumulations of CO₂ are observed is very similar to the Midale Beds in terms of whole rock chemistry, mineralogy, mineral chemistry and porosity distribution. In both cases, anhydrite-rich evaporates, sometimes contains authigenic K-feldspar, form aquitards which, in the case, of the Duperow appear to have prevented loss of CO₂ over a time frame that may extend as long as 50 m.y. (*cf.* Lake and Whittaker, 2003). These accumulations, coupled with the striking similarity between these lithologies, provide support for the security of CO₂ injection at Weyburn.

3. Acknowledgements

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